Thermally Stable Calcium-Aluminum Bulk Amorphous Metals With Low Mass Density

Related Applications

This application claims priority under 35 USC §119(e) to US Provisional Application Serial Nos. 60/477,605, filed June 11, 2003, 60/490,806, filed July 29, 2003 and 60/524,506, filed November 24, 2003, the disclosures of which are incorporated herein by reference.

US Government Rights

This invention was made with United States Government support under an Air Force Office of Scientific Research Contract No. F33615-01-2-5217 awarded by the Defense Advance Research Projects Agency. The United States Government has certain rights in the invention.

Background

Bulk-solidifying amorphous metal alloys (a.k.a. bulk metallic glasses) are those alloys that can form an amorphous phase upon cooling the melt at a rate of several hundred degrees Kelvin per second or lower. Amorphous alloys usually exhibit certain superior properties than their crystalline counterparts with the same or similar compositions, such as tensile or compressive strength, wear resistance and corrosion resistance as well as oxidation resistance. As promising structural materials, the study of light-metal-based amorphous alloys has grown in the past two decades. To date, light-metal-based amorphous alloys have been successfully prepared in several alloy systems, including Mg-TM-RE (wherein TM represents late transition metals, such as Cu and Ni, and RE represents rare earth metals, such as Y and La), Al-TM-RE (including Ni, Co and Fe as the TM element and Gd and Y as the RE element), Al-Cu-Mg-Ni and recently reported Ca-Cu-Mg alloys.

Table 1 lists the glass transition temperature Tg, onset temperature of crystallization Tx, reduced glass transition temperature Trg (defined as glass transition temperature over the melting point of the alloy in Kelvin), calculated mass

density (grams per cubic centimeter) and glass formability of several representative light-metal-based amorphous alloy compositions. The calculated mass density was obtained by assuming no volume contraction or expansion when alloying the component elements together. The glass formability was characterized by the diameter in millimeters of the cast cylinder-shaped rod with a fully amorphous structure or by the thickness of the ribbon-shaped samples with a fully amorphous phase for those alloys whose glass formability is not high enough to form bulk amorphous samples.

Table 1. Summary of representative light-metal-based amorphous alloy compositions, together with Tg, Tx, Trg, calculated mass density and glass formability.

Composition (at.%)	Tg (^{0}C)	Tx (^{0}C)	Trg	Calculated Mass Density	Glass Formability
$Al_{87}Ni_7Gd(Y)_6$	N/A	210		3.18-3.58	200-300 μm
$Al_{85}Ni_7Gd(Y)_8$	250	280	0.45	3.24-3.76	100-150 μm
$Mg_{60}Cu_{30}Y_{10}$	160	210	0.60	3.40	6 mm
$(Al_{75}Cu_{17}Mg_8)_{95}Ni_5$	N/A	167		3.55	100 μm
$Ca_{67}Mg_{19}Cu_{14}$	114	134	0.60	1.92	2 mm
$Ca_{57}Mg_{19}Cu_{24}$	131	167	0.64	2.24	≥ 4 mm

All the alloys listed in **Table 1**, except $Al_{85}Ni_7Gd(Y)_8$ alloys, which unfortunately is not a bulk glass former, exhibit quite low thermal stability. Their Tg, if observable, is much less than 200^{0}C, with their Tx being at most near 200^{0}C. From the practical point of view, the low thermal stability of the light-metal-based bulk amorphous alloys mentioned above has limited their application as structural materials. It is an attractive idea to develop light-metal-based amorphous alloys which simultaneously exhibit a large glass formability and a high thermal stability useful for structural applications.

Summary of Various Embodiments of the Invention

The present invention is directed to a new class of bulk amorphous alloys based on calcium and aluminum that exhibit large glass formability and high thermal stability and thus are useful for structural applications. With variation of the composition, the mass density of the CaAl-based bulk amorphous alloys ranges from

1.74 to 2.50 grams/cc, which is among the lowest values reported for amorphous metals. The thermal stability of CaAl-based amorphous alloys, having Al content of about 25-30 atomic percent, is much higher than those of the Ca-based Al-free amorphous alloys ($Tg = 180\text{-}240^0C$), while exhibiting glass formability that allows for the preparation of cast amorphous rods having a diameter of at least 1mm.

Brief Description of the Drawings

Fig. 1. represents a photograph of an as-cast 9 mm diameter amorphous rod of $Ca_{55}Al_{10}Mg_{15}Zn_{15}Cu_5$ alloy.

Fig. 2. illustrates an x-ray diffraction pattern from exemplary sample pieces (each of total mass about 1 gram) obtained by crushing a 2mm as-cast rods of a bulk amorphous $Ca_{56.5}Al_{28.5}Mg_{10}Cu_5$ alloy.

Fig. 3. illustrates differential scanning calorimeter (DSC) curves representing the crystallization and melting behavior of high Al content CaAl-based representative alloys as marked in the figure.

Fig. 4. represents enlarged DSC curves of Fig. 3 showing the glass transition phenomenon of the high Al content CaAl-based representative alloys.

Fig. 5. illustrates differential scanning calorimeter (DSC) curves representing the crystallization and melting behavior of low Al content CaAl-based representative alloys with compositions marked in the figure.

Detailed Description of Embodiments

Definitions

In describing and claiming the invention, the following terminology will be used in accordance with the definitions set forth below.

As used herein, the term "reduced glass temperature (Trg)" is defined as the glass transition temperature (Tg) divided by the liquidus temperature (Tl) in K.

As used herein, the term "supercooled liquid region (ΔTx)" is defined as crystallization temperature minus the glass transition temperature.

As used herein, the term "calcium-based alloy" refers to alloys wherein calcium constitutes a major component of the alloy. Typically, the calcium-based

amorphous alloys of the present invention have a Ca content of approximately 50% or greater, however, the Ca content of the present alloys may comprise anywhere from 35% to 75% calcium.

As used herein, the term "amorphous alloy" is intended to include both completely amorphous alloys (i.e. where there is no ordering of molecules/atomic packing), as well as partially crystalline alloys containing crystallites that range from nanometer to the micron scale in size.

Embodiments

Aluminum-based amorphous alloys have been successfully prepared in several alloy systems, however the previous described light metal-based bulk glass alloys suffer the disadvantage of exhibiting low thermal stability. Applicants have discovered a new class of bulk amorphous alloys based on calcium and aluminum that simultaneously exhibit large glass formability and high thermal stability and thus are useful for structural applications. Experimentally it was found that binary Ca-Al alloys, close to the Ca-rich eutectic composition range, are able to form bulk cylinder-shaped amorphous rods with a diameter up to 1 mm. This is believed to be the first report of the formation of bulk amorphous alloys in a binary metal system. With the further introduction of Cu, Ag, Mg and/or Zn, the glass formability of the alloys is improved and the diameter of the cast amorphous rods varies from 3 to 9 mm, depending on the Al content of the alloys.

In one embodiment of the present invention a calcium-based aluminum amorphous alloy comprising at least 50% calcium is prepared using commercial grade material to create an alloy that can be processed into cylinder samples having a diameter of 1.0 millimeter or greater. In one embodiment the calcium-based aluminum amorphous alloys of the present invention exhibit a Tg of at least 170°C. In one embodiment calcium-based amorphous alloys comprise at least 50% calcium and 20-35% aluminum and exhibit a Tg greater than 200°C. In another embodiment a calcium-based amorphous alloy is provided, comprising at least 50% calcium and 10-20% aluminum, that can be cast as an amorphous rod having a continuous diameter of about 3 to about 9mm and exhibiting a Tg greater than 110°C. In one embodiment the

bulk-solidifying Ca-based amorphous alloys of the present invention are completely amorphous. Since the synthesis-processing methods employed by the present invention do not involve any special materials handling procedures, they are directly adaptable to low-cost industrial processing technology.

In accordance with one embodiment of the present invention, a calcium-based amorphous alloy with enhanced glass formability and high thermal stability properties is provided wherein the alloy is represented by the formula:

$$Ca_{(100-t)}Al_xCu_yAg_nZn_mMg_pNi_r \qquad \textbf{I}$$

wherein

x, y, n, m, p and r are atomic percentages, wherein

x is a number selected from about 5 to about 35;

y is a number selected from 0 to about 15;

n, m, p and r are independently a number selected from 0 to about 20, wherein y + n + m + p + r is less than 30; and

t is the sum of x, y, n, m, p and r, with the proviso that t is a number selected from about 25 to about 55. In accordance with one embodiment, an alloy of the general formula **I** is provided wherein x is a number selected from about 25 to about 40, r is 0, and y + n + m + p is less than 20. In accordance with one embodiment, an alloy of the general formula I is provided wherein x is a number selected from about 30 to about 40 and y, n, m, r and p are each 0.

In accordance with another embodiment, a calcium-based amorphous alloy is provided wherein the alloy is represented by the formula:

$$Ca_{(100-t)}Al_xQ_g \qquad \textbf{II}$$

wherein Q is an element selected from the group consisting of Cu, Ag, Zn and Mg;

x is a number selected from about 25 to about 35;

g is a number selected from 0 to about 15; and

t is the sum of x and g.

In accordance with one embodiment, a calcium-based amorphous alloy is provided wherein the alloy is represented by the formula:

$$Ca_{(100-t)}Al_xCu_yAg_nZn_mMg_p \qquad \textbf{III}$$

wherein

x, y, n, m and p are atomic percentages, wherein

x is a number selected from about 25 to about 35;

p is a number selected from about 5 to about 15;

n, m and y are independently a number selected from 0 to about 20, wherein y + n + m + p is less than 30; and

t is the sum of x, y, n, m and p, with the proviso that t is a number selected from about 25 to about 55.

In accordance with one embodiment, an alloy of the general formula **III** is provided wherein x is a number selected from about 25 to about 35, y and m are independently a number selected from 0 to about 10, n is a number selected from 0 to about 15, p is a number selected from 0 to about 20, and t is the sum of x, y, n, m and p, with the proviso that t is a number selected from about 25 to about 55.

In a further embodiment a calcium-based amorphous alloy that exhibit a Tg greater than 200°C is provided wherein the alloy has the general structure of formula **III**. More particularly in one embodiment an alloy of the general formula **III** is provided wherein x is a number selected from about 27 to about 32, y and n are independently a number selected from 0 to about 5, m is 0, p is about 10 to about 20, and t is a number selected from about 43 to about 47. In another embodiment an alloy of the general formula **III** is provided wherein x is a number selected from about 27 to about 30, y and n are independently a number selected from 0 to about 5, m is 0, p is about 10 to about 15, and t is a number selected from about 43 to about 44. In another embodiment an alloy of the general formula **III** is provided wherein x is a number selected from about 27 to about 30, n is a number selected from 0 to about 10, y and m are both 0, p is about 10 to about 15, and t is a number selected from about 43 to about 44. In another embodiment an alloy of the general formula **III** is provided wherein x is a number selected from about 27 to about 32, n, y and m are each 0, p is about 10 to about 15, and t is a number selected from about 42 to about 45.

In another embodiment a light-metal-based amorphous alloy is provided that has superior glass formability, allowing for the formation of amorphous

rods with diameters ranging from greater than 2mm to about 9mm. Such calcium-based amorphous alloys are represented by the general formula:

$$Ca_{(100-t)}Al_xCu_yAg_nZn_mMg_pNi_r \qquad \mathbf{I}$$

wherein

x, y, n, m, p and r are atomic percentages, wherein

x is a number selected from about 5 to about 15;

p is a number selected from about 5 to about 15;

r is a number selected from 0 to about 10;

n, m and y are independently a number selected from 0 to about 20, wherein y + n + m is less than about 21; and

t is the sum of x, y, n, m, p and r, with the proviso that t is a number selected from about 35 to about 55. In accordance with one embodiment a calcium/aluminum-based amorphous alloy is provided that has superior glass formability, wherein the alloy is represented by formula **I** wherein x is a number selected from about 5 to about 15, y is a number selected from 0 to about 15, n is 0, m is a number selected from about 10 to about 20, p is a number selected from about 10 to about 15, r is a number selected from 0 to about 10, and t is a number selected from about 35 to about 50.

In accordance with one embodiment, a calcium-based amorphous alloy is provided wherein the alloy is represented by the formula:

$$Ca_tAl_xQ_yZn_mMg_p \qquad \mathbf{IV}$$

wherein Q is Cu or Ni;

t, x, y, m and p are atomic percentages, wherein

t is a number selected from about 50 to about 60;

x is a number selected from about 10 to about 15;

y is a number selected from about 5 to about 10;

m is a number selected from about 10 to about 20; and

p is a number selected from 10 to about 15.

In accordance with one embodiment a calcium/aluminum-based amorphous alloy is provided that has superior glass formability, wherein the alloy is represented by formula **IV** wherein t is a number selected from about 55 to about 60, x is about 10, y

is a number selected from 0 to about 10, m is a number selected from about 10 to about 20 and p is a number selected from about 10 to about 15.

The CaAl-based bulk amorphous alloys of the present invention can be formulated to generate higher thermal stability or higher glass formability properties by manipulating the aluminum content of the alloy. More particularly, "high Al" content alloys, containing 25-35 atomic percent Al, exhibit a thermal stability much higher than those of the Ca-based Al-free amorphous alloys. Typically, the high Al amorphous alloys exhibit a Tg of greater than 200°C and a Tx ranging from about 220 to about 270°C. "Low Al" content alloys, containing 5-15 atomic percent Al, are able to form amorphous rods having a diameter of at least 3mm and up to about 9 mm. These low Al content Ca-Al amorphous alloys exhibit a Tg ranging from 120 to 150^0C and Tx from 150 to more than 200°C, and thus they exhibit greater glass formability at the sacrifice of some of the thermal stability. However, these low Al amorphous alloys are better suited in GFA than previously described Ca-alloys.

With variation of the composition, the mass density of the CaAl-based bulk amorphous alloys ranges from 1.74 to 2.50 grams/cc, which is among the lowest values reported for amorphous metals. Preliminary measurement of the CaAl-based amorphous alloys shows that the microhardness is in the range of 200-240/DPH. According to the empirical relationship between the microhardness value and the mechanical strength, these amorphous alloys are expected to exhibit a fracture tensile strength around 700-800 MPa. This value is about 40% higher than that of the previously disclosed Ca-based Al-free amorphous alloys, where a compressive fracture strength of 545 MPa was reported for the alloy $Ca_{57}Mg_{19}Cu_{24}$. The good combination of large glass formability, low mass density, high thermal stability and mechanical properties indicates that the CaAl-based amorphous alloys could be a promising structural material where comprehensive properties are required.

The present alloys may be devitrified to form amorphous-crystalline microstructures, or infiltrated with other ductile phases during solidification or melting of the amorphous alloys in the supercooled-liquid region, to form composite materials, which can result in strong hard products with improved ductility for structural applications. In accordance with one embodiment of the invention, the

alloys can be made to exhibit the formation of quasi-crystals upon cooling at a rate somewhat slower than the critical cooling rate for glass formation. In this case, the alloy can solidify into a composite structure consisting of quasi-crystalline precipitates embedded in an amorphous matrix. In this way, high strength bulk quasi-crystalline materials can be produced and thus the range of practical applications is extended. For example, quasi-crystalline materials typically have very low coefficients of friction and high hardness, making them useful for bearing applications.

In accordance with one embodiment of the present invention, an article of manufacture is provided wherein the article comprises a light-metal-based amorphous alloy represented by the formula:

$$Ca_{(100-t)}Al_xCu_yAg_nZn_mMg_pNi_r \qquad \textbf{I}$$

wherein

x, y, n, m, p and r are atomic percentages, wherein

x is a number selected from about 5 to about 15;

p is a number selected from about 5 to about 15;

r is a number selected from 0 to about 10;

n, m and y are independently a number selected from 0 to about 20, wherein y + n + m is less than about 21; and

t is the sum of x, y, n, m, p and r, with the proviso that t is a number selected from about 35 to about 55. In accordance with one embodiment a calcium/aluminum-based amorphous alloy is provided that has superior glass formability, wherein the alloy is represented by formula I wherein x is a number selected from about 5 to about 15, y is a number selected from 0 to about 15, n is 0, m is a number selected from about 10 to about 20, p is a number selected from about 10 to about 15, r is a number selected from 0 to about 10, and t is a number selected from about 35 to about 50.

In accordance with another embodiment, an article of manufacture is provided wherein the article comprises a calcium-based amorphous alloy represented by the formula:

$$Ca_tAl_xQ_yZn_mMg_p \qquad \textbf{IV}$$

wherein Q is Cu or Ni;

t, x, y, m and p are atomic percentages, wherein

t is a number selected from about 50 to about 60;

x is a number selected from about 10 to about 15;

y is a number selected from about 0 to about 10;

m is a number selected from about 10 to about 20; and

p is a number selected from 10 to about 15.

In accordance with another embodiment, an article of manufacture is provided wherein the article comprises a CaAl-based amorphous alloy represented by the formula:

$$Ca_{(100-t)}Al_xCu_yAg_nZn_mMg_p$$

wherein

x, y, n, m and p are atomic percentages, wherein

x is a number selected from about 25 to about 35;

n is a number selected from about 0 to about 20;

m and y are independently a number selected from 0 to about 15,

p is a number selected from about 0 to about 20; and

t is the sum of x, y, n, m and p, with the proviso that t is a number selected from about 30 to about 50.

Owing to the good glass formability, CaAl-based alloys can be produced into various forms of amorphous alloys, such as thin ribbon samples by melt spinning, amorphous powders by atomization, amorphous rods, sheets and/or plates by casting. The casting can be carried out using conventional injection casting, die casting, squeeze casting, suction casting and strip casting as well as other state-of the-art casting techniques currently employed in research labs and industries. Owing to the existence of a distinct supercooled liquid region, it is very promising to utilize the formability of the CaAl-based amorphous alloys in the supercooled liquid region to form desired shapes of frames and parts without further machining.

The combination of low mass density, high thermal stability and mechanical properties as well as good glass formability make the present CaAl-based amorphous alloys promising structural materials having applications where high

comprehensive properties are required. The alloys can be used in a variety of applications including use as coatings to provide oxidation and/or corrosion resistant layers and use as structural materials under extreme environments. Ceramic particles or fibers and/or refractory metal particles can be blended with atomized CaAl-based alloy powders, and by extrusion, used to produce composite materials for structural applications. Alternatively, the present alloys may be devitrified partially to form amorphous-crystalline composite materials.

The present CaAl-based amorphous alloys may be used in many application areas. Some of the products and services to which the present invention can be implemented include, but are not limited thereto 1) vehicle (land-craft and aircraft) frames and parts, 2) engineering, construction, and medical materials and tools and devices, 3) laminate composite: laminate with other structural alloys (e.g. Mg, Al, Fe, and Ti to name a few) for aerospace applications, 4) other utilizations that require the combination of specific properties realizable by the present Ca-based amorphous alloys. CaAl-based metallic glasses may also have other useful functional applications in addition to their mechanical properties. As important as its potential practical application, from the scientific point of view, CaAl-based amorphous alloys (especially the binary Ca-Al alloy), provide an ideal system to study the fundamental issues related to glass formability of alloy systems.

Example 1

Preparation of CaAl-Based Amorphous Alloys

Ingot Preparation

Alloy ingots were prepared by melting mixtures of high purity elements in an induction furnace. Boron-nitride-coated graphite crucibles are used as the melting boat in the preparation of alloy ingots. For the Cu and Ag-containing alloys, Cu and Ag elements are placed on the top of the raw materials. Because Cu and Ag are materials with the highest melting points in these alloy system, they will be the last ones to be melted during melting. Arranging the elements in this way allows direct observation of the melting of Cu and/or Ag, which then react with the melted material, assuring a homogeneous composition.

Glass formability

The amorphous samples were produced preliminarily via conventional copper mold casting, which is realized by injecting the alloy melt into a cylinder-shaped cavity inside a water-cooled copper block. Thermal transformation data were acquired using a Differential Scanning calorimeter (DSC). The designed CaAl-based amorphous alloys exhibit a reduced glass transition temperature Trg in the range 0.56-0.63 and a supercooled liquid region ΔT in the range 20-50 ^{0}C. The alloys of this invention can be cast into amorphous rods with diameters reaching up to 3-9 mm, depending on the Al content employed. A picture of the 9 mm as-cast amorphous rod of $Ca_{55}Al_{10}Mg_{15}Zn_{15}Cu_5$ alloy is shown in Fig. 1. The amorphous nature of the cast rods is verified by x-ray diffraction and DSC measurement (see Figs 2 through 5).

Example 2

High Al content (25-35 at.%) Ca-Al-based alloys

With Al as the main additive, the strong interaction of Al with Ca and the unique network microstructure between Ca and Al atoms give the high thermal stability of the designed amorphous alloys. Introducing additional elements such as Mg, Cu, Ag, Zn, further improves the glass formability of the alloys, resulting in binary (CaAl), ternary (CaAlCu, CaAlAg, CaAlMg, CaAlZn), quaternary (CaAlCuAg, CaAlMgCu, CaAlMgAg, CaAlMgZn and CaAlCu(Ag)Zn) and quinary (CaAlMgCuAg, CaAlMgCuZn and CaAlMgAgZn) alloys. Exemplary alloys include those represented by the following formulas (in atomic percent)

Binary alloys

$Ca_{100-x}Al_x$

where $32 \leq x \leq 37$

Ternary alloys

$Ca_{100-x-y}Al_xCu(Ag,Mg,Zn)_y$

where $27 \leq x \leq 35$, $0 \leq y \leq 20$

Quaternary alloys

$Ca_{100-x-y}Al_x(A_aB_b)_y$

where $27 \leq x \leq 35$, $0 \leq y \leq 17$, $0 \leq a,b \leq 100$, and AB represents combinations of CuAg, MgCu, MgAg, MgZn, CuZn or AgZn.

Quinary alloys

$Ca_{100-x-y-z}Al_xMg_y(A_aB_b)_z$

where $27 \leq x \leq 35$, $5 \leq y \leq 15$, $5 \leq z \leq 15$, $0 \leq a,b \leq 100$, AB represents combinations of CuZn or AgZn.

These alloys are found to exhibit a Tg = 180-240 ^{0}C, Tx = 200-270 ^{0}C, and Trg =0.56-0.61 (applicable only for those alloys that show a glass transition). Typical XRD pattern of the cast amorphous rods is shown in Fig. 2. Curves of differential scanning calorimeter (DSC) analysis showing the glass transition, crystallization and melting behavior are given in Figs. 3 and 4. It is interesting to note that binary Ca-Al amorphous alloys possess the highest thermal stability. However, further introduction of Cu, Ag, Mg and/or Zn increase the glass formability of this alloy system. The diameter of the cast rods with a fully amorphous structure increases from 1 mm for binary alloys to 3 mm for multinary alloys. The addition of Ag helps to extend the supercooled liquid region, with $\Delta T = 48^0C$ for $Ca_{60}Al_{30}Ag_{10}$. A number of typical amorphous alloys are listed in Table 2, together with their Tg (if observable), Tx and the glass formability characterized by the diameter (in mm) of the cast rod with a fully amorphous structure.

Example 3

Low Al content Ca-Al-based alloys

The low Al content CaAl alloys are composed of at least four components. With decreasing the Al content to the range of 5 to 15 atomic percent, and at the same time, mainly increasing Zn content to replace Al, the designed alloys are given in the following formula:

$Ca_xAl_{5\text{-}15}Mg_yZn_zCu_s(Ni)_t$

where $50 < x < 65$, $10 < y < 15$, $10 < z < 20$, $0 \leq s < 15$ and $0 \leq t < 10$.

The thermal stability of the obtained amorphous alloys was decreased when compared to the high Al content alloys, with Tg ranging from 120 to 150°C and Tx from 150 to 200°C or above. However, the glass formability was greatly improved, resulting in alloys that can be cast into 9 mm diameter amorphous rods. Fig. 1 shows a picture of the as-cast 9mm amorphous rod of $Ca_{55}Al_{10}Mg_{15}Zu_{15}Cu_5$ alloy. Fig. 5 presents a series of DSC curves of the low Al content CaAl alloys where the glass transition, crystallization and melting behavior are shown. A number of typical amorphous alloys are listed in Table 3, together with their Tg (if observable), Tx and the glass formability characterized by the diameter (in mm) of the cast rod with a fully amorphous structure.

Both high and low Al content Ca-Al alloys possess a low mass density. The calculated mass density of the alloys ranges from 1.74 to 2.50 gram/cc. The calculation is done by neglecting the possible volume contraction and expansion effect when alloying these component elements together.

Preliminary measurement indicated that the microhardness of the invention amorphous alloys is in the range 200-240 DPH. The fracture strength has not been evaluated yet. According to the empirical rule between the microhardness value and the mechanical property, the fracture tensile strength is expected to be on the level of 700-800 MPa.

Table 2. Thermal data obtained from differential thermal analysis (DTA) scans of High Al content Ca-based bulk amorphous alloys.

Composition (at.%)	Tg (^{0}C)	Tx (^{0}C)	Diameter of amorphous rod	Calculated mass density (gram/cc)
$Ca_{66.4}Al_{33.6}$	255	267	1mm	1.74
$Ca_{55}Al_{30}Cu_{15}$	N/A	206	1mm	2.17
$Ca_{60}Al_{30}Cu_{10}$	225	244	1.5 mm	2.00
$Ca_{55}Al_{35}Cu_{10}$	N/A	244	1mm	2.05
$Ca_{65}Al_{30}Cu_{5}$	N/A	242	1 mm	1.85
$Ca_{63}Al_{32}Cu_{5}$	230	257	2mm	1.87
$Ca_{60}Al_{30}Ag_{10}$	210	258	2mm	2.20
$Ca_{63}Al_{32}Ag_{5}$	230	254	1.5mm	1.96
$Ca_{60}Al_{30}Mg_{10}$	235	250	2mm	1.74
$Ca_{60}Al_{30}Zn_{10}$	225	257	1.5mm	1.99
$Ca_{55}Mg_{10}Al_{30}Cu_{5}$	N/A	216	1mm	2.02
$Ca_{58}Al_{32}Mg_{10}$	240	266	1.5mm	1.75
$Ca_{55}Al_{30}Mg_{15}$	240	262	1mm	1.75
$Ca_{58}Al_{27}Mg_{15}$	230	255	1.5mm	1.73
$Ca_{56.5}Al_{28.5}Mg_{15}$	230	255	1.5mm	1.74
$Ca_{56}Al_{29}Mg_{5}Cu_{10}$	N/A	206	1mm	2.01
$Ca_{53}Al_{27}Mg_{10}Cu_{10}$	N/A	197	1mm	2.02
$Ca_{56.5}Al_{28.5}Mg_{10}Cu_{5}$	220	247	3mm	1.87
$Ca_{56.5}Al_{28.5}Ag_{15}$	210	238	1mm	2.45
$Ca_{60}Al_{30}Cu_{5}Ag_{5}$	215	242	1mm	2.10
$Ca_{56.5}Al_{28.5}Ag_{10}Cu_{5}$	170	194	1mm	2.35
$Ca_{62.5}Al_{31.5}Cu_{4}Ag_{2}$	220	250	1.5mm	1.93
$Ca_{60}Al_{30}Ag_{8}Cu_{2}$	205	248	1.5mm	2.16
$Ca_{53}Al_{27}Mg_{10}Ag_{10}$	205	230	1.5mm	2.22
$Ca_{56.5}Al_{28.5}Mg_{10}Ag_{5}$	215	242	3mm	1.97
$Ca_{54.5}Al_{27.5}Mg_{10}Ag_{8}$	205	238	2mm	2.12
$Ca_{55.5}Al_{29.5}Mg_{10}Ag_{5}$	216	248	2mm	1.98
$Ca_{57.5}Al_{27.5}Mg_{10}Ag_{5}$	220	255	2mm	1.96
$Ca_{54.5}Al_{30.5}Mg_{10}Ag_{5}$	220	257	1.5mm	1.99
$Ca_{53.5}Al_{31.5}Mg_{10}Ag_{5}$	220	257	1.5mm	2.00
$Ca_{53}Al_{27}Mg_{15}Ag_{5}$	210	228	1.5mm	1.98
$Ca_{53}Al_{27}Mg_{15}Cu_{5}$	220	240	1.5mm	1.88
$Ca_{53}Al_{27}Mg_{13}Ag_{7}$	200	224	1mm	2.07
$Ca_{53}Al_{27}Mg_{17}Ag_{3}$	220	245	1mm	1.88
$Ca_{56.5}Al_{28.5}Mg_{10}Zn_{5}$	230	250	1.5mm	1.87
$Ca_{56.5}Al_{28.5}Mg_{5}Zn_{5}Cu_{5}$	215	235	1mm	2.00
$Ca_{56.5}Al_{28.5}Mg_{5}Zn_{5}Ag_{5}$	210	240	1.5mm	2.10

Table 3. Thermal data obtained from differential thermal analysis (DTA) scans of Low Al content Ca-based bulk amorphous alloys.

Composition (at.%)	Tg (^0C)	Tx (^0C)	Diameter of amorphous rod	Calculated mass density (gram/cc)
$Ca_{60}Al_5Mg_{15}Zn_{20}$	127	159	7 mm	2.11
$Ca_{55}Al_{10}Mg_{15}Zn_{20}$	137	189	5 mm	2.17
$Ca_{55}Al_{10}Mg_{15}Zn_{15}Cu_5$	127	159	9 mm	2.17
$Ca_{55}Al_{10}Mg_{15}Zn_{10}Cu_{10}$	120	138	7 mm	2.18
$Ca_{55}Al_{10}Mg_{15}Zn_{17}Cu_3$	135	163	7 mm	2.17
$Ca_{55}Al_{10}Mg_{15}Zn_{12.5}Cu_{7.5}$	116	137	7 mm	2.17
$Ca_{55}Al_{10}Mg_{15}Zn_{15}Ni_5$	131	169	7 mm	2.16
$Ca_{50}Al_{15}Mg_{15}Zn_{15}Cu_5$	136	189	3 mm	2.22
$Ca_{55}Al_{15}Mg_{10}Zn_{15}Cu_5$	141	200	3 mm	2.19
$Ca_{55}Al_{15}Mg_{15}Zn_{10}Cu_5$	130	148	3 mm	2.06